THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

DEVELOPMENT OF A MANUFACTURING PROCEDURE FOR LOW-LITHIUM, LOW-URANIUM CONTENT FILTER PAPER

Project 3101

Report Twelve

A Status Report

to

DEPARTMENT OF THE AIR FORCE
1155th TECHNICAL OPERATIONS SQUADRON (HQ. COMD.)
McCLELLAN AFB, CALIFORNIA

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SUMMARY

The use of ammonium bicarbonate alone or in conjunction with ammonium fluoride, ammonium chloride, or hydrochloric acid to purify IPC-1478 paper was tested. The uranium and lithium contents were less satisfactory than those in paper processed with ammonium carbonate and hydrofluoric acid. Two batches of IPC-1478 paper were purified and were treated with Kronisol (dibutoxyethyl phthalate).

Five series of 6-inch handsheets were made in an all-plastic apparatus from purified pulp. The results support the possibility of making IPC-1478 paper on a practical scale from suitably engineered equipment.

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INTRODUCTION

Efforts to produce IPC-1478 paper with the specified goals for uranium and lithium contents were continued. Experiments included leaching commercially-made paper with chemical agents, and the making of handsheets in an all-plastic apparatus. Both processes appear to be useful in reaching an acceptable quality of paper.

DISCUSSION

PURIFICATION OF IPC-1478 PAPER

In view of the success of leaching commercially-made paper with ammonium carbonate and hydrofluoric acid (1), other chemicals were tested. IPC-1478 paper from Roll No. 22, Series N (untreated with Kronisol[a]) was cut into squares and stacked with similar squares of Hercules PS-57, cotton linter pulp. In a succession of experiments ammonium bicarbonate alone or with other chemical agents (ammonium fluoride, ammonium chloride, or hydrochloric acid) was used to leach the stacks of pulp and paper. The results, listed in Table I, showed that for Samples 311-318 none of the chemical agents was as effective as the ammonium carbonate-hydrofluoric acid process (see Samples 342-347) in the removal of uranium and lithium[b]. These differences may be related, in part, to the somewhat lower pH (approximately pH 8) of the bicarbonate than that of the carbonate (approximately pH 9). However, the results for pulp Samples 313 and 316 were not significantly different from those for 341, and for 340, Table II. These observations are consistent with

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[a] Kronisol is dibutoxyethyl phthalate manufactured by C. P. Hall Co., Chicago, Ill.

[b] Comparisons of samples, treated and untreated with Kronisol, should be corrected to the same basis weight since the uranium and lithium contents of Kronisol are practically negligible. Data in this report were not corrected.

TABLE I

PURIFIED IPC-1478 PAPER AND HERCULES PULP (PS-57)

Uranium and lithium contents[a]

Sample No. 3101-		Uranium 8/5	Uranium ng/g (ng/ml)[c]	Lithium, ng/g (ng/ml)[c]	Description
Purification of IPC-1478 Paper[b], with Ammonium Bicarbonate — Squares (15.5 by 15.5 cm) of IPC-1478 paper, Series N, was stacked on 3 squares of Hercules PS-57 pulp and topped with 6 squares; total weight of stack, 151 g. The stack was leached with 1.5 liters of 0.1M ammonium bicarbonate, washed with 2 liters of water, and dried. The cycle was repeated once.					
311	A	123	0.25	2.62	IPC-1478 paper after first cycle
	B			2.63	
312	A			1.94	IPC-1478 paper after second cycle
	B	122	0.36	1.85	
313	A	121	0.21	0.38	Pulp squares adjacent to Sample 312
	B			0.33	
Purification of IPC-1478 Paper[b], with Ammonium Bicarbonate and Ammonium Fluoride — The above experiment (Samples 311 and 312) was repeated except that the reagent was 0.1M in each of the salts.					
314	A			(2.78)	IPC-1478 paper after first cycle
	B			(2.76)	
	C	124	0.22	2.42	
	D			2.26	
315	A			2.03	IPC-1478 paper after second cycle
	B	126	0.17	2.33	
	C	125	0.15	2.15	
316	A			0.55	Pulp squares adjacent to Sample 315
Purification of IPC Paper[b], with Ammonium Bicarbonate and Hydrochloric Acid — A stack of IPC-1478 paper and Hercules pulp was leached once with 1.5 liters of ammonium bicarbonate, 2 liters of water, 1.5 liters of 0.1M hydrochloric acid, and 3 liters of water.					
317	A			1.87	IPC-1478 paper, purified
	B	125	0.15	1.72	
	C	127	0.21	2.21	
Purification of IPC-1478 Paper[b], with Ammonium Bicarbonate and Ammonium Chloride — The above experiment (Sample 317) was repeated except that the reagent was a mixture of the salts, 0.1M in each.					
318	A	126	0.20	(3.17)	IPC-1478 paper, purified
	B			2.25	
	C			2.14	
	D			2.31	

See end of table for footnotes.

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TABLE I (Continued)

PURIFIED IPC-1478 PAPER AND HERCULES PULP (PS-57)

Uranium and lithium contents[a]

Sample No. 3101-		Uranium 8/5	Uranium ng/g (ng/ml)[c]	Lithium, ng/g (ng/ml)[c]	Description
Purification of Hercules, PS-57 Pulp — Disks of pulp (3101-266) from handsheet-making (Samples 319-338) were stacked and leached by percolation through one cycle with 0.1M ammonium carbonate and 0.1M hydrofluoric acid.					
341	A	132	0.050	0.26	Purified pulp
	B			0.47	
Purification of IPC-1478 Paper[b] — An amount of 51 squares (8 1/8 by 8 1/8 inches), 290 g, was stacked between squares of Hercules pulp to form a stack with a total weight of 582 g. The stack was leached in 2 cycles with 0.1M ammonium carbonate and 0.1M hydrofluoric acid, and treated with 30 g Kronisol/100 g untreated paper.					
342	A	137	0.055	0.86	Upper section, Kronisol distributed by centrifugation
	B			1.04	
343	A	139	0.075	1.01	Lower section, Kronisol distributed by centrifugation
	B			1.15	
344	A			0.88	Upper section, Kronisol solution in 95% ethyl alcohol added; paper dried
	B	135	0.069	1.18	
345	A			1.10	Lower section, Kronisol solution in 95% ethyl alcohol added; paper dried
	B			0.91	
Purification of IPC-1478 Paper[b]. Modified Procedure — The stack was composed of 287 g of paper and 337 g of pulp. The stack was leached by the above procedure (342-345) except that, in the first cycle, leaching with 0.1M hydrofluoric acid was the first step [see Experimental].					
346	A			0.98	Upper section, Kronisol distributed by centrifugation
	B	116	0.061	0.95	
347	A			0.86	Lower section, Kronisol distributed by centrifugation
	B	136	0.055	0.88	
348		131	0.00052	0.052	Triple deionized water; collected 2-14-74
349		153	0.00056	0.0042	Special distilled water, triple distilled in glass from alkaline potassium permanganate; collected 2-27-74

[a] Data supplied in letters dated March 27 and April 8, 1974, from Capt. Frank Grosso to E. E. Dickey.
[b] All IPC-1478 paper was cut from Roll No. 22, Series N.
[c] Uranium and lithium contents of water samples are expressed as ng/ml.

TABLE II

HANDSHEETS MADE ON AN ALL-PLASTIC SHEET MOLD

Uranium and lithium analyses[a]

Sample No. 3101-		Uranium 8/5	Uranium ng/g (ng/ml)[b]	Lithium, ng/g (ng/ml)[b]	Description
Handsheets were made on an all-plastic sheet mold equipped with a closed white water loop. Purified pulp, 3101-266, in 2.7 g lots, was dispersed in 700-800 ml of water under mechanical stirring with a stainless steel stirrer. The dispersion was diluted to 4 liters in triple-deionized water at pH 9 (with ammonium carbonate) and made into a handsheet. The sheet was couched from the mold with a disk of the purified pulp (3101-266) and dried. Five series of handsheets were made in succession with the water replaced for each series.					
			Series 319-321		
319	A	137	0.23	2.16	Sheets 1-12
	B			3.09	
	C			2.47	
	D			2.86	
320	A			1.77	Sheets 13-25
	B	133	0.22	2.46	
321	A	134	0.0020	0.0222	White water after Sheet No. 25;
	B			0.0164	total volume of water, 10 liters
			Series 323-325		
323	A			0.96	Sheets 1-11
	B	136	0.11	1.17	
324	A			0.77	Sheets 12-22
	B	144	0.12	(1.45)	(Higher than normal 8/5 for uranium)
	C			0.96	
	D			1.24	
325	A	126	0.08	0.94	Sheets 23-33
	B			0.75	
326	A			0.011	White water after Sheet No. 33;
	B	130	0.0016	0.010	total volume, 10 liters
			Series 327-330		
327	A	131	0.078	0.79	Sheets 1-12
	B			0.75	
328	A	131	0.091	1.08	Sheets 13-24
	B			0.87	
329	A			1.37	Sheets 25-36
	B	133	0.12	0.83	
330	A	132	0.0015	0.0092	White water after Sheet No. 36;
	B			0.0098	total volume, 11 liters

See end of table for footnotes.

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TABLE II (Continued)

HANDSHEETS MADE ON AN ALL-PLASTIC SHEET MOLD

Uranium and lithium analyses[a]

Sample No. 3101-		Uranium 8/5	Uranium ng/g (ng/ml)[b]	Lithium, ng/g (ng/ml)[b]	Description
			Series 331-334		
331	A			1.06	Sheets 1-12
	B	132	0.090	0.95	
332	A			0.69	Sheets 13-24
	B	130	0.078	0.77	
333	A			0.90	Sheets 25-36
	B	135	0.097	0.82	
334	A	134	0.0012	0.0094	White water after Sheet No. 36;
	B			0.0128	total volume, 11 liters
			Series 335-338		
335	A			0.76	Sheets 1-12
	B	131	0.077	0.56	
336	A			0.74	Sheets 13-24
	B	123	0.12	0.66	
337	A	125	0.11	0.82	Sheets 25-36
	B			0.73	
338	A	132	0.0019	0.0126	White water after Sheet No. 36;
	B			0.0103	total volume, 11 liters
322	A	136	0.0007	0.0058	Triple-deionized water collected
	B			0.0084	on 12-11-73
339	A	131	0.0006	(0.013)	Triple-deionized water collected
	B			0.006	on 1-22-74
340	A	125	0.057	0.48	Control, purified PS-57 pulp
	B			0.34	(from 3101-266)

[a] All analytical data were obtained at McClellan AFB, MCLC, and were transmitted in letters dated March 27 and April 8, 1974, from Capt. Frank Grosso to E. E. Dickey.
[b] Uranium and lithium contents of water samples are expressed as ng/ml.

the results generally obtained on Project 3101 which indicate that a fraction of the lithium appears to occupy inaccessible sites in the cellulose fibers. Furthermore, somewhat larger amounts are retained by commercially-made paper than by the pulp from which it was made (2).

HANDSHEETS MADE IN ALL-PLASTIC EQUIPMENT FROM PURIFIED PULP

An apparatus for the demonstration of papermaking was available temporarily for use on Project 3101. A bronze wire was replaced by a plastic papermaking wire thereby removing the only metal to which the pulp would be exposed except for a stainless steel stirrer used to disperse the pulp. The equipment consisted of the plastic sheet mold, a closed loop white water system, and a motor-driven pump.

Five series of 6-inch handsheets were made in the apparatus using purified Pulp 266 (sampled during the series as 340). No attempt was made to use scrim on these handsheets in order to eliminate this possible source of lithium in the papermaking process. A pH of 9 was maintained by the addition of ammonium carbonate. The apparatus was rinsed at the end of each series and recharged with triple deionized water. The analytical results are listed in Table II.

By inspection of the uranium content for each series, it was evident that all of the handsheets were below the specified goals of < 0.3 ng U/g, and the trend was downward with each succeeding series except for the fifth series (335-337). The trend for lithium dropped consistently throughout the series, but never reached the specified level of < 0.4 ng Li/g. Likewise, the white water at the end of each series (No. 321, 326, 330, 334, and 338), which included

an unknown amount of fines (1) showed a similar decline with successive series. It seems plausible that these trends indicate a gradual scouring of uranium and lithium from the apparatus. It seems equally plausible that eventually an equilibrium would be reached whereby a low level of these elements would be maintained in such handsheets (3).

The consistently low level of lithium in the handsheets of the fifth series, No. 335-337, support the possibility of making IPC-1478 paper with lithium levels approaching the specified goal. The success of such a process would probably depend upon the use of new, all-plastic equipment, of water similar to the triple-deionized used in these experiments, and of drying equipment supplied with dust-free air. Such an operation would provide, also, for the purification of pulp prior to the papermaking operation.

FUTURE WORK

1. Work is in progress to complete the purification of squares (20 by 20 inches) of IPC-1478 paper, Series N, with the application of Kronisol to the purified paper.

2. Tetramethylammonium hydroxide will be used to raise the pH of solutions for the leaching of pulp and paper samples. More highly alkaline solutions than those used to date may favor the removal of lithium, especially in the percolation schemes.

EXPERIMENTAL

PURIFICATION OF IPC-1478 PAPER, SERIES N

311 to 313. Ammonium Bicarbonate

An amount of 60 g of IPC-1478 paper, Series N, Roll 22, in the form of squares 15.5 by 15.5 cm, was stacked on three squares of Hercules PS-57 pulp, and the stack was topped with six squares of the pulp; total weight of the stack, 151 g. The stack was leached by percolation with 1.5 liters of 0.1M ammonium bicarbonate, washed with 2 liters of water, pressed under a rubber sheet, and dried in filtered air at room temperature. The cycle was repeated. A sample of the IPC paper was packaged after the first cycle as 311, and after the second cycle as 312. Pulp squares which had been adjacent to the paper were packaged after the second cycle as 313. The analytical data are summarized in Table I.

314 to 316. Ammonium Bicarbonate and Ammonium Fluoride

The general procedure, as described above, was repeated except that the stack of pulp and paper was leached in two cycles with 0.1M ammonium bicarbonate and ammonium fluoride. The stack was washed with 1 liter of water between the reagents and with 2 liters of water after the ammonium fluoride treatment. The following samples were packaged: No. 314, paper after the first cycle; No. 315, paper after the second cycle; and No. 316, pulp adjacent to the paper after the second cycle. Analytical data are summarized in Table I.

317. Ammonium Bicarbonate and Hydrochloric Acid

The general procedure, as described above, was repeated except that the stack of pulp and paper squares was leached once, only, with 0.1M solutions

of ammonium bicarbonate and hydrochloric acid. The purified paper, Sample No. 317, was analyzed and the data are listed in Table I.

318. Ammonium Carbonate and Ammonium Chloride

The general procedure, as described above, was repeated except that the stack of pulp and paper was leached in one cycle, only, with a solution containing a mixture of ammonium bicarbonate and ammonium chloride, 0.1M in each salt. The stack was washed with 3 liters of water, and the purified paper, Sample 318, was analyzed and the data are listed in Table I.

319 to 340. Preparation of Handsheets from Purified Pulp (266) in an All-Plastic Sheet Mold

A sheet mold is available at the Institute for demonstrations of papermaking to visitors. The device was designed to form a circular sheet of paper, 6 inches in diameter on a bronze wire. All other parts are made of plastics, including the lining of a circulating pump. To eliminate contamination due to the bronze wire it was replaced with a "plastic wire." The sheet mold was designed to hold approximately 12 liters of water and was equipped with a closed loop for recycling the white water.

Purified pulp (266), 2.7 g, was dispersed in 1.2 liters of white water at pH 9 (with ammonium carbonate) under mechanical stirring with a stainless steel stirrer in a plastic beaker, the dispersion was diluted to 4 liters in the sheet mold, and the sheet was formed. The sheet was couched from the wire with two sheets of the purified pulp (266), an accumulated stack was pressed under a rubber dam, and the sheets were separated and dried.

A total of five series of handsheets was made with a complete change of water between each series. From each set, samples for analysis were assembled along with a white water sample, and are listed in Table III. The analytical data are listed in Table II.

341. Purification of Pulp

Disks of purified pulp from Lot 266 were used in the above handsheet series, 319-340. The used disks were assembled into a stack and were leached by percolation with 4 liters of 0.1M ammonium carbonate, 4 liters of water, 4 liters of 0.1M hydrofluoric acid, and 12 liters of water. The stack was pressed and dried in the usual way. A sample designated as 341 was submitted for analysis, Table I.

342 to 345. Purification of IPC-1478 Paper, Series N

An amount of 290 g (51 squares, 20.5 by 20.5 cm) of IPC-1478 paper, Series N, Roll 22, was stacked with 292 g of squares of Hercules pulp, PS-57, 10 squares on top the paper and 5 on the bottom of the stack. The stack was weighted and was leached by percolation in two cycles:

First Cycle

3 liters 0.1M ammonium carbonate

3 liters water

3 liters 0.1M hydrofluoric acid

6.5 liters water

Stack pressed to 1757 g (33.2% consistency)

Dried in sets of three squares in filtered air at room temperature.

TABLE III

FIVE SERIES OF HANDSHEETS MADE IN AN ALL-PLASTIC SHEET MOLD FROM PURIFIED PULP (3101-266)

Sample No. Assigned, 3101-	Weight, g	Description
		Series 319-322
319	45	Sheets 1-12
320	26	Sheets 13-25
321	--	White water after Sheet No. 25; total volume, 10 liters
322	--	Triple-deionized water collected on 12-11-73
		Series 323-326
323	31	Sheets 1-11
324	31	Sheets 12-22
325	34	Sheets 23-33
326	--	White water after Sheet No. 33; total volume, 10 liters
		Series 327-330
327	34	Sheets 1-12
328	30	Sheets 13-24
329	33	Sheets 25-36
330	--	White water after Sheet No. 36; total volume, 11 liters
		Series 331-334
331	32	Sheets 1-12
332	34	Sheets 13-24
333	33	Sheets 25-36
334	--	White water after Sheet No. 36; total volume, 11 liters
		Series 335-338
335	32	Sheets 1-12
336	32	Sheets 13-24
337	30	Sheets 25-36
338	--	White water after Sheet No. 36; total volume, 11 liters

Second Cycle

3 liters 0.1M ammonium carbonate

3 liters water

3 liters 0.1M hydrofluoric acid

12 liters water

Stack pressed to 2319 g (24.8% consistency)

Dried in sets of three squares in filtered air at room temperature.

Alternate sheets of the paper were stacked separately to form two substacks which were placed in polyethylene bags. One substack was treated with Kronisol (no solvent present), and the other was treated with a solution of 42 g of Kronisol dissolved in 200 ml of 95% ethyl alcohol. Both packages were centrifuged in laundry-type (spin-drier) equipment for 15 minutes. The sample without solvent was placed on a table under 15 kg of weights to favor the evenness of distribution of Kronisol by capillary action.

The substack treated with the alcohol solution of Kronisol was removed from the PE bag, and the paper was dried in sets of three for one hour in a hood at room temperature.

Both substacks were divided into "upper" and "lower" sections, packaged, and labelled as shown in Table IV. Analytical data are listed in Table I.

TABLE IV

PURIFIED SAMPLES OF IPC-1478 PAPER TREATED WITH KRONISOL

Sample No. 3101-	Weight, g	Description	
342	80	Upper section	Kronisol distributed by centrifugation
343	74	Lower section	
344	75	Upper section	Kronisol solution in 95% ethyl alcohol added; paper dried
345	72	Lower section	

346-347. Purification of IPC-1478 Paper

The general procedure described above for Samples 342-345 was modified somewhat for the purification of a similar stack of squares, 287 g of paper and 337 g of pulp. The stack was leached in two cycles:

First Cycle

Four liters each in succession of

0.1M hydrofluoric acid, water,

0.1M ammonium carbonate, water, and

0.1M hydrofluoric acid, followed by

12 liters of water.

The stack was pressed and dried in the usual way.

Second Cycle

Four liters each in succession of

0.1M ammonium carbonate, water, and

0.1M hydrofluoric acid, followed by

12 liters of water.

Again the stack was pressed and dried in the usual way.

The paper (not the pulp) was reassembled, in order, into a stack and Kronisol (34 g/100 g of airdry paper) was poured onto the paper. After thirty minutes, the stack, contained in a sealed PE bag, was centrifuged in the laundry-type equipment for 15 minutes. The stack was then separated into top and bottom halves and the bottom sheet of the bottom half was placed between the top two sheets of the top half. Thus, the halves were combined into a single stack which was centrifuged and again divided into an upper half, No. 346 and a lower half, No. 347. Analytical data are listed in Table I.

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348-349. Water Samples

Sample 348 was triple-deionized water collected on 2-14-74 and should be representative of the water used to process the samples of pulp and paper described in this report. Sample 349 was collected on 2-27-74 for comparison with Sample 348. It was taken from a supply of water which was triple distilled in glass and included one stage to which alkaline potassium permanganate was added. Analytical data are listed in Table I.

LITERATURE CITED

1. Project 3101, Report Ten, January 22, 1974.

2. Project 3101, Report Seven, August 22, 1973, p. 17.

3. Project 3101, Report Nine, November 9, 1973, p. 8-10.

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